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Ultrafast spectroscopy of energetic materials and energetic mechanical processes

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13. ABSTRACT ***(Maximum 200 Words)***

The goal of this project is to develop a fundamental understanding of fast mechanical processes at a molecular level. It is believed this fundamental research will lead to a clearer understanding of energetic mechanical processes relevant to the AFOSR mission and in the broader world as well. These include: (1) impact initiation of energetic materials; (2) mechanical failure by debonding, cracking or spallation; (3) lubrication dynamics of high speed parts; (4) fast combustion of metal particle/oxidizer composites. These processes are induced by laser generated shock waves, laser heating, or specific vibrational pumping with tunable femtosecond mid-IR pulses. They are probed with vibrational spectroscopy of the bulk molecules or nonlinear optical techniques that are interface or surface selective. It is the combination of high speed detailed molecular probes and fast mechanical processes that makes this work unique.

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Title of project: Ultrafast spectroscopy of energetic materials and energetic mechanical processes

Reporting period: 15 Jan 2000 -- 30 Nov. 2002

2-3. Status of Effort (Objectives have changed)

The goal of this project remains the development of a fundamental understanding of fast mechanical processes at a molecular level. We have phased in an additional objective, which involves understanding the fundamental mechanisms of energetic materials produced by nanotechnology. It is believed this fundamental research will lead to a clearer understanding of energetic mechanical processes relevant to the AFOSR mission, which are also found everywhere. These include: (1) impact initiation of energetic materials; (2) mechanical failure by debonding, cracking or spallation; (3) lubrication dynamics of high speed parts; (4) high-speed exoergic chemistry of finely dispersed metal particles. At the present time experimental techniques to study these problems at the molecular level (nanometers, femtoseconds) are lacking. There are several reasons for this lack. The simplest explanation is that the only tool presently capable of studying material dynamics at this level is an optical tool—the femtosecond laser. But light is better suited to studying electronic processes and is not well-suited for studying mechanical processes. In our work, we have concentrated on three ways of using light pulses to create fast mechanical perturbations: resonant mid-IR vibrational pumping, laser-driven shock waves, and laser flash-heating. These perturbations are followed by fast IR or Raman probing to study the vibrational transitions of mechanically perturbed molecules or materials. Mid-IR absorption creates a highly nonequilibrium vibrational population whose relaxation is relevant to all highly energetic chemical processes. Shock waves create high pressure, large amplitude structural perturbations, high temperatures and large strain rates. Using ultrafast shock compression, we can reproducibly on command initiate energetic chemistry, cracking, debonding and spallation, and produce stress on liquids at solid interfaces that mimics the stress felt in high speed engines. Laser flash heating is used to heat metal nanoparticles embedded in oxidizing matrices. The hot metal particles can then undergo fast energetic oxidization chemistries.

There are three main experimental set-ups used in this work: (1) the picosecond flash-heating set-up (which also generates nanoshocks), which uses coherent anti-Stokes Raman probing (CARS) probing; (2) the vibrational sum-frequency generation and fast IR set-up, which uses a femtosecond laser for shock generation or flash-heating, and either IR-visible sum-frequency generation (SFG) to probe surface dynamics, or IR absorption to probe chemistry in bulk samples, and (3) the 3D energy transfer set up, which uses femtosecond IR pumping and incoherent Raman probing to study molecular mechanical energy transfer processes in condensed phases.

With the nanoshock CARS set up, we have completed an exciting study of shock compression of materials with nanostructure. We have engineered a model system consisting of a polymer, PMMA, with a large network of ~100 nm diameter pores. Shock compression of porous materials is poorly understood and interesting because compression of porous materials makes more heat. Pore compression is associated with hot spot formation that initiates heterogeneous energetic materials. In our experiments, we measured two important features. We measured how the shape of the shock front is altered by passing through a porous medium. We use a fast spectroscopic shock gauge involving detecting the CARS spectrum of a thin layer of anthracene. We generate a very steep shock front, propagate it through a few microns of nanostructured material and then use the anthracene gauge to detect the change in shape of the

shock front. We also measured real time compression of the voids, by using CARS to detect vibrational transitions of a dye probe inside the porous medium. The results support the viscoplastic model of pore collapse.

This set-up has also been used to study nanoenergetic materials. The principal system consisted of nanometric Al particles in a nitrocellulose (NC) oxidizer matrix. Several other materials have also been investigated, consisting of different combinations of size-selected Al and B nanoparticles, NC and poly-tetrafluoroethylene (PTFE) oxidizers. After flash heating we have detected a burst of emission which has been time and spectrally resolved. The duration of the emission burst represents the energy release rate. We have used CARS to monitor the chemical reactions between hot Al and NO2 groups from NC, which represents the onset of the initiation process. Finally we have studied reaction propagation through space, by separately measuring time constants for chemical reactions between Al and its nearby surrounding shell of NC, and for chemical reactions occurring in the NC that lies between hot Al nanoparticles.

The SFG technique is a high-sensitivity and high-selectivity method for measuring the vibrational spectra of molecules at interfaces. Because this is a 3-wave mixing technique, the signal vanishes entirely in centrosymmetric media. Thus it is specifically sensitive to molecules at interfaces. Extremely high spatial resolution can be obtained. In our studies of alkyl molecules tethered to gold surfaces, SFG selectively sees the terminal $-CH_3$ group of the alkyl chains. This means we can use laser light—typically a few μm in wavelength, to selectively observe processes with a spatial resolution of ~1.5Å. We are working to exploit this technique to study dynamics occurring at sharply rising shock fronts, and a variety of other mechanical surface processes such as crack generation and propagation, spallation, and dynamic lubrication and wear at moving interfaces. These experiments have proven difficult. So far we have successfully detected shock fronts moving through these alkyl chains with very high time resolution. In addition we are surveying other material systems to find the best model materials that will give good results with high signal-to-noise and help us solve important problems in the area of fast mechanical processes. Some possibilities being studied now include the interface between metallic Al and Al_2O_3, the interface between Al and various self-assembled monolayers, corrosion inhibiters on copper, and water-metal and oil-metal interfaces.

The SFG apparatus is simultaneously used for flash-heating of nanoenergetics with IR probing. The concepts are similar to the CARS probe experiments described above. However with CARS, which is an insensitive probing technique, we can only observe the disappearance of the most abundant chemical species, for instance NO_2 in NC. IR probing is more promising, since the cross-section is orders of magnitude greater. However the laser needed to do IR is much more complicated than the CARS system, since CARS uses visible light. We would like to simultaneously monitor NO_2 disappearance plus the appearance of new chemical species containing Al. We send a broad-band IR pulse through the flash-heated sample and then we sum the IR with visible light in a material that has a large SFG cross-section. By converting the IR probe into visible, it can be detected by a very sensitive optical detector. So far we have some preliminary data where we can monitor NO_2 disappearance using some different transitions than in the CARS work, which is not yet a big breakthrough, but we do see evidence for the growth of new chemical species as well. These initial results are promising and in the next contract period we expect a lot from this apparatus.

The energy transfer work continues to be successful. Vibrational energy transfer plays several important roles in energetic materials, as described in my recent chapter on fast events in energetic materials, but the fundamental mechanisms remain poorly understood. Thus this is an important area for fundamental studies needed to develop models of energetic material performance. We use an IR laser to pump a molecular vibration (e.g. C-H or OH stretch). A series of anti-Stokes Raman spectra at different times shows us how the energy leaves the initial state and flows through the rest of the molecule. This technique is a 2D vibrational spectroscopy. Varying the IR wavelength to excite different vibrations makes it a 3D technique. We have studied several simple liquids including nitromethane, acetonitrile, water and various alcohols. In our work on alcohols, we used molecules of the form, $OH\text{-}(CH_2)_n\text{-}CH_3$. We pumped the OH group and monitored the arrival of vibrational energy at the terminal $-CH_3$. By varying the number of intermediate –CH2- groups (or some branched carbon groups) we were able to measure the time needed for vibrational energy to move across a single carbon atom. These were the first real-time measurements of vibrational energy moving down a molecular chain, representing a significant breakthrough in our understanding of vibrational energy.

4. Accomplishments/new findings

- Real time spectroscopic observation of pore collapse
- 3D vibrational spectroscopy of molecular liquids
- Real time measurements of vibrational energy flow down molecules
- Real time measurements of nanoenergetic material initiation, ignition and propagation
- Shock front detection with 1.5Å spatial resolution
- Comprehensive review of fast processes in energetic materials
- High spatial resolution laser transfer of rheological liquids in the jetting regime

5. Personnel Supported

Number of Contract/Grant Co-Investigators*

Faculty 1	Post Doctorates 3	Graduate Students 2	Other 0

1. Dana D. Dlott, PI, leads the project.
2. Dr. Andrei Pakoulov works on the multidimensional spectroscopy project
3. Dr. Zhaohui Wang also works on the multidimensional spectroscopy project
4. Dr. Yanqiang Yang leads the nanoenergetic materials project
5. Mr. Kurt Vance, an undergraduate in chemical engineering, made high-speed images of aluminum particle combustion
6. Dr. Alexi Lagoutchev leads the SFG project
7. Mr. James Patterson, a graduate student, works on the SFG project
8. Dr. Shufeng Wang works on fast IR spectroscopy of nanoenergetic materials

6. Publications Related to Aforementioned Contract/Grant

1. Name of Journal: Annu. Rev. Phys. Chem.

Title of Article: Ultrafast spectroscopy of shock waves in molecular materials

Authors: Dana D. Dlott

Volume 50 Pages 251-78 Month Published: May 2000. Year: 1999

2. Name of Journal: Acc. Chem. Res.

Title of Article: Nanoshocks in molecular materials

Authors: Dana D. Dlott

Volume 33 Pages 37-45 Month Published: Jan. 2000 Year: 2000

3. Name of Journal: Ph.D. Dissertation

Title of Article: Vibrational energy relaxation in liquids

Authors: Lawrence K. Iwaki, Jr.

Volume Pages 129 Month Published: Jan. Year: 2000

4. Title of Article: Three-dimensional spectroscopy of vibrational energy relaxation in liquid methanol

Authors: L. K. Iwaki, Jr., and Dana D. Dlott

Volume 104 Pages 9101-9112 Month Published: Oct 2000 Year: 2000

5. Name of Journal: Chemical Physics (special issue on multidimensional spectroscopy)

Title of Article: Vibrational energy redistribution in polyatomic liquids: 3D infrared-Raman spectroscopy

Authors: Dana D. Dlott

Volume 266 Pages 149-166 Month Published: May Year: 2001

6. Journal of Applied Physics

Title of Article: Real time spectroscopy of shock wave nanopore collapse

Authors: Selezion A. Hambir, Hackjin Kim, Dana D. Dlott and Robert B. Frey

Volume 90 Pages 5139-5146 Month Published: Nov. 2001 Year: 2001

7. Name of Journal: J. Photochem. Photobiol. A: Chemistry (special issue on laser ablation)

Title of Article: Ultrafast microscopy of laser ablation of refractory materials: ultra low threshold stress-induced ablation

Authors: Serguei G. Koulikov and Dana D. Dlott

Volume 145(3) Pages 183-194 Month Published: Dec Year: 2001

8. Name of Journal: Shock Waves

Title of Article: Ultrafast vibrational spectroscopy of nanoshock planar propagation

Authors: Yanqiang Yang, Selezion A. Hambir and Dana D. Dlott

Volume 12 Pages 129-136 Month Published: Sept Year: 2002

9. Name of Journal: Shock Waves

Title of Article: Ultrafast high repetition rate absorption spectroscopy of polymer shock compression

Authors: Hackjin Kim, Selezion A. Hambir and Dana D. Dlott

Volume 12 Pages 79-86 Month Published: July Year: 2002

10. Name of Journal: Appl. Surf. Sci.

Title of Article: Ultra-low threshold laser ablation investigated by time-resolved microscopy

Authors: Dana D. Dlott

Volume 197-198 Pages 3-10 Month Published: Sept Year: 2002

11. Name of Journal: Appl. Surf. Sci.

Title of Article: Plume and jetting regimes in a laser based forward transfer process as observed by time-resolved optical microscopy

Authors: D. Young, R. C. Y. Auyeung, A. Piqué, D. B. Chrisey and Dana D. Dlott

Volume 197-198 Pages 181-187 Month Published: Sept Year: 2002

12. Name of Journal: Science

Title of Article: Watching Vibrational Energy Transfer in Liquids with Atomic Spatial Resolution

Authors: Zhaohui Wang, Andrei Pakoulev and Dana D. Dlott

Volume 296 Pages 2201-2203 Month Published: June Year: 2002

13. Name of Journal: Chem. Phys. Lett.

Title of Article: Fast spectroscopy of energy release in nanometric explosives

Authors: Shufeng Wang, Yanqiang Yang, Zhaoyong Sun and Dana D. Dlott

Volume 368 Pages 189-194 Month Published: Jan Year: 2003

14. Name of Journal: J. Phys. Chem. B

Title of Article: Fast spectroscopy of laser-initiated nanoenergetic materials

Authors: Yanqiang Yang, Zhaoyong Sun, Shufeng Wang and Dana D. Dlott
Volume in press Pages Month Published: Year: 2003

15. Name of Journal: Chem. Phys. Lett.

Title of Article: Vibrational relaxation and spectral evolution following ultrafast OH stretch excitation of water

Authors: Andrei Pakoulev, Zhaohui Wang and Dana D. Dlott

Volume Pages Month Published: Jan Year: 2003

16. Name of Book: *Energetic materials: Initiation, Decomposition and Combustion*, P. Politzer, ed.

Title of Article: Fast molecular processes in energetic materials

Volume in press Pages Month Published: Year: 2003

7. Interactions/Transitions

a. Conferences attended and presentations made

141. (*invited*) Department of Chemistry, University of California Los Angeles (Feb. '00), "Two-dimensional vibrational spectroscopy of liquids".

142. (*invited*) Department of Chemistry, University of California Berkeley (Feb. '00), "Two-dimensional vibrational spectroscopy of liquids".

143. (*invited*) Department of Chemistry, Stanford University (Feb. '00), "Two-dimensional vibrational spectroscopy of liquids".

144. (*invited*) 8th International Symposium on Molecular Processes in Small Time and Space Domains, Nara, Japan (Mar. '00), "Ultrafast microscopy of laser surface modification".

145 (*invited*) Department of Chemistry, Toyama University, Toyama, Japan (Mar. '00), "IR-Raman measurements of vibrational relaxation in liquids:"

146. (*invited*) American Physical Society National Meeting, Minneapolis, MN (Mar. '00), "Vibrational relaxation in liquids via two-dimensional vibrational spectroscopy".

147. (*invited*) American Chemical Society National Meeting, San Francisco, CA (Mar. '00), "Ultrafast spectroscopy of nanoshocks in molecular materials".

148. (*invited*), University of Wisconsin, Department of Chemistry, (May '00) "Vibrational relaxation in liquids via 3D vibrational spectroscopy".

149. (*invited*) International Workshop on Warm Dense Matter, Vancouver, BC (May '00), "Ultrafast spectroscopy of laser-driven shocks in molecular materials".

150. (*invited*) Gordon conference on Energetic Materials, New Hampton, NH (July '00), "Real time observation of hot spot formation in energetic materials".

151. American Chemical Society National Meeting, Washington, DC (Aug. '00), "Vibrational energy relaxation in molecular liquids".

152. Air Force Workshop on High Energy Density Matter, Salt Lake City, UT (Oct. '00), "Real-time vibrational spectroscopy of nanostructured energetics".

153. (*invited*) Sixth International Conference on Molecular Reaction Dynamics in Condensed Phases, Laguna Beach, Ca (Feb. '01), "Three dimensional vibrational spectroscopy of molecular liquids".

154. (*invited*) American Physical Society March Meeting, Seattle, WA (Mar. '01), "Three dimensional vibrational spectroscopy of molecular liquids".

155. (*invited*) Department of Chemistry, Case Western Reserve University, Cleveland, OH (Mar. '01), "Ultrafast spectroscopy of shock waves in molecular materials".

156. (*invited, plenary lecture*), 2001 International Conference on Time-resolved Vibrational Spectroscopy, Okazaki, Japan (May 2001), "Ultrafast three dimensional vibrational spectroscopy of vibrational energy relaxation in liquids".

157. (*invited*) DARPA High Energy Density Materials and Nanotechnology Workshop, Washington, DC (Aug. '01), "Engineered nanometric energetic materials".

158. (invited) University of Illinois Department of Ceramics, Urbana, IL (Sept. 2001), "Laser photothermal ablation studied by ultrafast microscopy: fundamental mechanisms of ultra low threshold ablation"

159. (*invited*), International Conference on Laser Ablation 2001, Tsukuba, Japan (Oct. 2001), "Laser photothermal ablation studied by ultrafast microscopy: fundamental mechanisms of ultra low threshold ablation"

160. (*invited*) University of Illinois Department of Chemistry, Urbana, IL (Nov. 2001), "Three-dimensional vibrational spectroscopy".

161. American Chemical Society National Meeting, (Mar. 2002), Ultrafast vibrational sum frequency generation spectroscopy of lubricants at moving metal interfaces.

162. (*invited*) Emory University Department of Chemistry, Atlanta, GA (Apr. 2002), "Three-dimensional spectroscopy of vibrational energy transfer in liquids".

163. (*invited*) Georgia Institute of Technology, Department of Chemistry, Atlanta, GA (Apr. 2002), "Three-dimensional spectroscopy of vibrational energy transfer in liquids".

164. (*invited*) Air Force Workshop on High Energy Density Matter, Waltham, MA (May. '02), "Fast vibrational spectroscopy of shock compression and combustion".

165. Gordon Conference on Energetic Materials, Tilton, NH (June '02), "Ultrafast laser spectroscopy of nanoenergetic materials".

166. (*invited*) Gordon Conference on Vibrational Spectroscopy, Newport, RI (July '02), "Three-dimensional spectroscopy of vibrational energy transfer in liquids".

167. (*invited*) Advanced Energetics Technology Exchange, Lawrence Livermore National Laboratory (Sept. '02), Livermore, CA, "Ultrafast spectroscopy of nanoenergetic materials".

168. (*invited*) Columbia University Department of Chemistry, (Sept. '02), New York, NY, "Three dimensional spectroscopy of vibrational energy transfer in liquids".

169. (*invited*) Yale University Department of Chemistry, (Sept. '02), New Haven, CT, "Three dimensional spectroscopy of vibrational energy transfer in liquids".

170. (*invited*) Wayne State University Department of Chemistry (Oct. '02), Detroit, MI, "Three dimensional spectroscopy of vibrational energy transfer in liquids".

171. (*invited*) Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Providence, RI (Oct. '02) "Three-dimensional spectroscopy of vibrational energy transfer in liquids".

172. (*invited*) *Coblentz Award Symposium,* Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Providence, RI (Oct. '02), "Three-dimensional spectroscopy of vibrational energy transfer in liquids".

173. (*invited*) Northwestern University Department of Chemistry (Nov. '02), Evanston, IL, "Three dimensional spectroscopy of vibrational energy transfer in liquids".

b. Consultative and advisory functions

b.1. Nominations committee for the American Physical Society Topical Group on Shock Compression of Condensed Matter.

b.2. Organized a symposium for the Aug. 2000 national meeting of the ACS, titled, "Chemistry in extreme conditions", with Dr. Bob Morris of AFRL.

b.3. Advisory editor for Applied Physics Letters and the Journal of Applied Physics, 2000-2002

b.4. Program committee for the 2003 APS International Conference on Shock Compression in Condensed Matter

b.5. Organized the Sixth International Conference on Molecular Reaction Dynamics in Condensed Matter

b.6. Member of panel tasked by ITRI Corp. with writing a report on worldwide status of molecular dynamics simulations of energetic materials

b.7. Consultant, Presstek, Inc.

b.8. Consultant, Optodot, Inc.

b.9. Consultant, Hanita Coatings, Hanita, Israel

b.10. Awards committee, American Chemical Society

b.11. University of Cyprus external Review of Applied Physics Department Faculty

c. Transitions

The work we did on ultrafast dynamics of near-IR absorbers has been transitioned to a start-up "Optodot". They intend to use near-IR absorbers for switching of fast optical signals on fiber optical networks. contact Dr. Steve Carlson, Optodot, Inc., scarlson@optodot.com.

The work we did on fast microscopy of laser transfer using rheological materials with co-workers at NRL has led to a patent application for high resolution transfer in the jetting regime. Contact Dr. H. D. Young, Naval Research Lab, hdyoung@ccs.nrl.navy.mil.

I have been working with researchers at Hanita Coatings on understanding the fundamental mechanisms of their new laser imaging materials. Contact: Dany Eisenstadt, R&D Manager, Hanita Coatings, Israel, dany@hanitacoatings.com

d. New discoveries, inventions or patent disclosures

Provisional application 60/327,733, "Jetting behavior in the laser forward transfer of rheological systems"

9. Honors and Awards

2001 Charles E. Ives Award from the Society for Imaging Science and Technology, 2001 (Dlott)